A HIGH ACTIVITY ZEOLITE-SUPPORTED
COBALT FISCHER-TROPSCH CATALYST

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Cobalt-based Fischer-Tropsch (F-T) catalysts are currently in favor because they are useful for processing methane-derived synthesis gas. There is an excess of methane at remote sites that might be economically converted into liquid hydrocarbons by a processing scheme based on F-T. Shell is purported to use a cobalt-based catalyst at their F-T plant in Sarawak. Exxon has worked extensively on supported cobalt F-T catalysts, particularly ones supported on titanium dioxide. Gulf-Chevron[1,2,3,4] and Exxon[5,6] have demonstrated that small amounts of ruthenium added to a supported cobalt F-T catalyst can cause catalyst activation.

Work done under a current DOE contract to UOP has resulted in a high activity, zeolite-supported, cobalt F-T catalyst (Contract No. DE-AC22-89PC8969). This catalyst resulted from impregnation of cobalt onto a Y zeolite-derived support. This support had been used in an earlier contract by workers from Union Carbide to prepare a less active cobalt F-T catalyst.

The support results from steaming and acid-washing Y zeolite. The purpose of the steaming is to create large amorphous pores in an otherwise crystalline matrix. The subsequent acid-washing removes alumina debris resulting from steaming thus clearing the remaining crystalline channels to facilitate diffusion of reactants and products to and from the catalyst active sites.

Compared to the catalyst developed during the previous Union Carbide contract, catalysts from the current work have higher cobalt levels. Thus Figure 1 illustrates the actual metals loading in some of the current catalysts compared to a reference catalyst remaining from the earlier work:

Catalysts prepared during this work were analyzed by scanning transmission electron microscopy (STEM). These analyses showed that at least some of the cobalt exists outside of the zeolite pores in crystallites attached to the external surface of the zeolite.

Short catalyst screening runs were performed in a fixed-bed pilot plant. In addition, one active catalyst was also evaluated in a longer run in a slurry autoclave pilot plant. Such a plant is useful for evaluating catalysts being developed for liquid phase F-T (LPFT) processing. The slurry autoclave run allowed determination of the catalyst deactivation rate and the change in selectivities as a function of time on stream.

When the fixed-bed reactor was used quartz sand was loaded with the catalyst to facilitate heat transfer since the F-T reactions are very exothermic. Prior to starting a run the metal oxide was reduced for two hours at 350° C with flowing hydrogen. Following reduction the reactor temperature was reduced until the inlet temperature was 211° C; the feed was then introduced. The feed rate was 4.9 NL/hour·g of cobalt and the plant pressure was 287 psig. The feed was a pure blend of hydrogen, carbon monoxide and argon purchased from Scott Specialty Gas Co. The feed molar ratio of hydrogen to carbon monoxide was two which is the same as that of a methane-derived synthesis gas. Argon was present as an internal standard for calculation of conversions and selectivities.

Figure 2 contains a tabular summary of Run 65 (reference catalyst from the previous contract) and Run 97 which used a catalyst containing about twice as much cobalt as the reference catalyst. The higher conversion during Run 97 was due, at least in part, to the de-facto higher operating temperature during this run (actual catalyst bed temperature profiles are in Figure 3). The high temperature resulted from the high density of active sites on the high cobalt catalyst which, in turn, caused extensive conversion near the inlet of the catalyst bed and, therefore, significant heat as well. Since cobalt-catalyzed F-T is very sensitive to temperature even a small difference between operating temperatures such as in Runs 65 and 97 can result in a significant conversion difference in

conversion. Subsequent runs with even higher cobalt catalysts used less catalyst, however, due to operational problems the amount used in these latter runs is as little as may be used.

A fresh sample of the catalyst used in Run 97 was bound with silica in preparation for use in the slurry autoclave pilot plant. For use in (LPFT) the powdery zeolite catalyst would have to be bound in order to form particulates large enough to have the required hydrodynamic properties. The bound catalyst was evaluated in the fixed bed reactor in Run 99. In this run, since the zeolite/cobalt was diluted by the silica, eighteen rather than thirteen grams of catalyst were used. The amount of cobalt in the reactor in Runs 97 and 99 was thus the same. The bound catalyst was also evaluated in the slurry autoclave pilot plant in Run 61. Eighteen grams of catalyst were also used in this run, however, 290 grams of (C_{30} oil) diluent were used. Since heat removal was expected to be much better in the slurry autoclave, the operating temperature was 221° C so that the performance data could be compared to that from Run 99 which operated at a _de-facto_ temperature that was above the target inlet of 211° C. For Run 99 the catalyst was reduced at the normal temperature but _ex-situ_ to the reactor. It was carefully transferred to the reactor under an inert atmosphere. The feed rate and operating pressure during the slurry autoclave run were the same as during Runs 97 and 99 (4.9 NL/hr·g Co and 287 psig, respectively). Performance data from Runs 97, 99 and 61 are compared in Figure 4.

After binding the catalyst was less active, possibly because the binder covered some of the catalyst active sites. Although the slurry autoclave was operated at a slightly higher temperature than the catalyst maximum temperature in Run 99, the conversions were similar in both runs. The methane selectivity during Run 61, however, was slightly lower than during Run 99. Unlike the screening runs in the fixed-bed reactor which were of short duration, Run 61 was four hundred hours long. During this run the conversions and selectivities appeared to approach a line out, however, some condition changes were made during the run making it difficult to absolutely judge the rate of catalyst deactivation. Additional slurry autoclave runs with high cobalt, Y zeolite-supported catalysts are needed.

Catalysts with levels of cobalt even higher than the Run 97 catalyst have been evaluated in the fixed-bed pilot under conditions identical to Run 97 except a lower level of catalyst was used. The results of these runs are summarized in Figure 5.

The catalyst loading used in Runs 110 and 123 is as low as practical. Obviously excess heat removal was still a problem at this low level. This means that increasing the cobalt level from eighteen to twenty-eight weight percent did result in the formation of quite a few additional active sites. The catalyst used in Run 110 contained ruthenium whereas the one used in Run 123 did not. Incorporation of small amounts of ruthenium into a cobalt catalyst composition should result in increased catalyst activity. This was not the case, however, the two very high cobalt catalysts above are merely first attempts. Perhaps the ruthenium is not yet well-dispersed into the cobalt. Modifications of the impregnation/activation procedures should be explored to see if additional activity can result from addition of ruthenium to the Y zeolite-supported catalyst composition. The catalyst bed maximum temperature was very high in Run 123, however, in spite of this the methane selectivity was not excessively high.

Apparently new active sites are formed as the level of cobalt on steamed, acid-washed Y zeolite is increased from 8 to 28 wt%. This is a significant observation because in LPFT processing the total volume of catalyst in the reactor will be critical. If a given volume of support can carry higher levels of catalytically active cobalt than previously thought possible, a superior LPFT catalyst will result. This is particularly true if these catalysts also retain the ability produce low levels of methane which, in fact, they do seem to do. Additional work with the very high cobalt-level catalysts is indicated. These should eventually be tested (after binding) in the slurry autoclave plant and compared to the catalyst evaluated in Run 61. However, before this additional compositions with small amounts of ruthenium should be prepared and screened in the fixed-bed plant. For LPFT processing catalyst activity is critical because of the low volume of catalyst that can be contained in an LPFT reactor, it is very important to find out if small amounts of ruthenium can activate the catalyst.

REFERENCES

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FIGURE 4

EVALUATION OF BOUND HIGH COBALT CATALYST: FIXED-BED AND SLURRY AUTOCLAVE TESTING

RUN NO.	LOADING CAT/DILUENT, g	MAX T °C	CO CONV, %	SELEC, MOL %		
				C_1	C_2	C_2^-
97	13/160	222	72	13	1.8	0.1
99	13/160	216	55	12	2.1	0.1
61	13/290	221	58	10	1.9	0.1

FIGURE 5

HIGH VS. VERY HIGH COBALT LEVEL CATALYSTS

RUN NO.	LOADING CAT/QUARTZ, g	MAX T °C	CO CONV %	SELEC, MOL%		
				C_1	C_2	C_2^-
97	13/160	222	72	13	1.8	0.1
110	6.5/166.5	220	86	8.6	1.2	0
123	6.5/166.5	230	90	10.5	1.5	0

6. E. Iglesia, S. Soled, R. Fiato and G. Via, J. Catal., 1993, 143, 345.

FIGURE 1

PROPERTIES: SUPPORTED OXIDES ON STEAMED Y ZEOLITE

CAT NO/RUN NO	SUPPORT SA^1/PV^2	METALS, WT%, AAS			
		Co	Mn	Zr	Ru
UNION CARBIDE/65	—	8.3	1.3	1.0	–
6827-81/97	582/0.56	17.6	2.0	1.6	1.0
6827-160/110	561/0.54	26.8	2.3	1.0	0.4
6827-161/123	588/0.55	28.7	1.8	1.1	–
1. m^2/g 2. cc/g					

FIGURE 2

PERFORMANCE OF THE REFERENCE TO A HIGH COBALT CATALYST

RUN NO.	LOADING CAT/QUARTZ, g	MAX T °C	CO CONV, %	SELEC, MOL %		
				C_1	C_2	$C_2^=$
65	13/160	213	40	7	0.6	0
97	13/160	222	72	13	1.8	0.1

FIGURE 3

CATALYST BED TEMPERATURE PROFILES DURING RUN 97

Temp, Deg C vs Inches

6 Hrs   48 Hrs   84 Hrs   120 Hrs